

# Supercritical Fluid Processing of Cosmetic Raw Materials

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When a substance is brought above a critical combination of temperature and pressure conditions, it exists in what is called the supercritical fluid (SF) state. The physical properties of such a SF are intermediate between those exhibited by a typical gas or liquid. In particular, a SF's density can be changed by varying the applied pressure on the fluid, from values typical of gases to near-liquid densities when the fluid is compressed by high pressures. At relatively high densities, a SF is capable of dissolving a variety of materials just as conventional liquids do.

Many advantages attend the use of supercritical fluids as extraction solvents.<sup>1,2</sup> The supercritical fluid extraction (SFE) process can produce a solvent-free product, can extract or fractionate a material under gentle conditions in a nonoxidative environment, and can be freely employed in the manufacturing of various chemicals since it is a separation process that causes little or no pollution.

These benefits are particularly evident when carbon dioxide ( $\text{CO}_2$ ) is employed as the fluid of choice, since its critical temperature ( $31^\circ\text{C}$ ) is close to ambient, and it is nontoxic and nonflammable. Carbon dioxide is also relatively cheap, and can be purified and recycled in a continuous extraction process.

An example of such a semi-continuous fluid recycle SFE system is shown by the schematic in Figure 1. The depicted system has been in operation at the National Center for Agricultural Utilization Research (NCAUR) for the past four years. It is capable of processing 12-14 pounds of material per run.

The fluid from the main  $\text{CO}_2$  supply is fed to the main compressor (a gas booster pump), where it is compressed to the required extraction pressure. The dense fluid is then diverted to one or more of the high pressure vessels (A, B or C) where the extraction is performed.

The compressed  $\text{CO}_2$ , laden with the extracted material, is conveyed as a one-phase system to the back-pressure relief valve (BPRV). There, the pressure is partially reduced, to precipitate the extracted matter from the fluid phase. The extracted material is collected in the re-

ceiver vessel (R) and the extraction fluid ( $\text{CO}_2$ ) is recirculated to the main compressor via a mass flowmeter.

Although fluid losses during processing are negligible, an auxiliary gas supply and compressor can be brought in-line to make up for the loss of harmless  $\text{CO}_2$  to the environment. Further details on this type of extraction system can be found in the literature.<sup>3</sup>

## Relevance to the Cosmetic Industry

The SFE process offers several distinct advantages for the processing of cosmetic raw materials. With the expansion of the "green" consumer movement, products utilizing supercritical carbon dioxide ( $\text{SC-CO}_2$ )-extracted ingredients offer some unique marketing possibilities. Such products can be touted as "the all-natural alternative," or "nature in its most concentrated form," or as "unlocking the essence of nature." Already, the food industry has hyped its supercritical fluid decaffeination process for coffee as "using only pure water and sparkling effervescence."

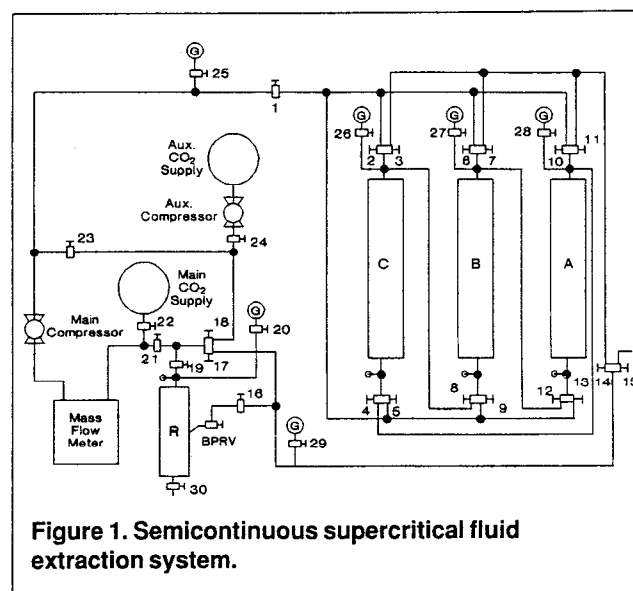


Figure 1. Semicontinuous supercritical fluid extraction system.

**Table I. Examples of cosmetic ingredients processed by SC-CO<sub>2</sub>**

Ascorbyl palmitate	Hops extracts
Avocado oil	Lanolin-based components
Cardamon oil	Lecithin
Carnauba wax	Fatty acids
Carotene	Glyceryl esters
Fatty alcohols	Shark liver oil
Cocoa butter	Terpenes and essential oils
Dimethicone	Tocopherols

But, in addition to the marketing bonus, SF processing offers the following benefits in the preparation of cosmetic raw materials:

- Elimination of solvent residuals in products
- Elimination of waste solvent disposal problems
- An ecologically compatible process
- Ability to tailor the properties of cosmetic ingredients
- Extraction and/or concentration of odoriferous components

Research conducted for the past few years has shown that SFE is an ideal technique for processing thermally labile compounds such as essential oils and spices.<sup>4,5</sup> Little alteration in the aroma quality of such moieties occurs when either supercritical (SC) or liquid CO<sub>2</sub> are used as solvents.<sup>6</sup> Several examples of cosmetic ingredients which have been processed by using SC-CO<sub>2</sub> are tabulated in Table I. The chemical nature of the listed ingredients can best be described as nonpolar, lipid-like, and very hydrophobic. One may therefore conclude that many compounds which have found a traditional niche in cosmetic formulations are amenable to extraction with SC-CO<sub>2</sub>.

Prior research conducted at this laboratory on the SFE of seed oils has shown a number of advantages inherent in the method. Extraction of such commodity oils with SC-CO<sub>2</sub> has resulted in lighter-colored oils, a better-tasting product, elimination of the traditional degumming step utilized in oil refining, lower refining losses, and solvent-free residual, protein-based meals for use in food compounding.<sup>7-9</sup> Unfortunately, SFE has been shunned by the seed-oil processing industry because of the very high capital equipment costs associated with the technique. However, Cygnarowicz-Provost<sup>10</sup> has recently shown that the cost of the final oil product using the SFE process is equivalent to that for oils obtained using traditional solvent extraction processes.

The economic benefits associated with the SFE of cosmetic components are even more favorable. These high cost-per-pound products are less sensitive to the capital investment costs inherent in their production processes. For this reason, we at NCAUR have explored the extraction with SC-CO<sub>2</sub> of a number of well-known, but expensive, cosmetic oils such as jojoba, avocado, macadamia nut, rose and evening primrose. More exotic substrates which we have also extracted with SC-CO<sub>2</sub> (on a smaller scale) include pistachio, juniper, kiwi and passion fruit.

SFE studies on these raw materials are not extensive.

**Table II. Supercritical CO<sub>2</sub> extraction of wheat bran and germ**

	Wheat bran	Wheat germ
Extraction conditions		
Pressure	8,000 psi	8,000 psi
Temperature	50°C	50°C
Time	5 hr	5 hr
Moisture content, %	11.4	10.7
Residual oil, %	—	1.3
Oil recovered, %		
of oil-bearing material	4.0	7.0
Description	wax	Light oil <sup>a</sup>

<sup>a</sup>Bland odor, 4.5% tocopherol

However, the solubility of the wax esters comprising jojoba oil in SC-CO<sub>2</sub> have been studied over a range of pressures and temperatures.<sup>3,11</sup> Research at NCAUR has resulted in residual oil levels of less than 1% in either flaked jojoba seed or press cake. Such oils can be further refined to produce a water-white product, at greater than a 99% yield.

SFE of related, but slightly differing, natural substrates often produces quite different products. For an example, let's look at the extraction of wheat bran versus wheat germ at 8000 psi and 50°C with SC-CO<sub>2</sub>. As shown in Table II, the extract derived from the bran substrate is a wax, while extraction of the wheat germ produced a lightly-colored oil of high tocopherol content. Either extract may be of value to the cosmetic formulator depending on the physical and chemical properties which are desired. Similar results for SC-CO<sub>2</sub> extraction of spent grain wax have been reported in this journal.<sup>12</sup>

### Principles and Limitations of SF Fractionation

Alteration of the physical properties or chemical composition of a SF extract depends on the degree of fractionation that one can obtain during the SFE process. SFE is inherently not a high-resolution fractionation process. To fractionate via SFE, one must have significant differences in the polarity or molecular weight of the components to be separated.

Despite these criteria, selective extractions have been reported in the literature. Isolation of caffeine and nicotine from coffee and tobacco are well-known SF processes. Essential oils can be separated from other lipid components in a variety of natural products, and fractionation by SFE of phospholipids in lecithin has also been cited.

For complex natural products which are used as ingredients in cosmetic products, SF fractionation cannot totally separate the natural substrate into its constituent components. Rather, the SF-based process will permit a partial fractionation of the constituents, thereby altering the chemical composition or physical properties of the final extract. For example, a stepwise increase in the extraction pressure alters the composition of jojoba oil according to the trend noted in Table III. This crude fractionation of the constituent wax esters produces fractions differing in boiling point and viscosity.

**Table III. Extraction/fractionation of jojoba oil at 80°C<sup>b</sup>**

Pressure (psig)	% Extraction by carbon number					
	36	38	40	42	44	46
3,000	3.5	12.8	36.8	41.4	4.6	0.3
5,000	2.3	10.4	35.2	44.9	6.2	0.5
7,000	1.7	8.9	34.7	46.8	6.9	0.7
9,000	1.4	7.5	32.6	49.3	8.2	1.1
11,000	0.8	5.4	28.6	53.0	10.4	1.5
Jojoba	1.7	8.3	32.4	48.2	8.3	0.8

<sup>b</sup>Extraction pressure increased stepwise

**Table IV. Concentration of tocopherols from soyflakes by SFE**

Fraction No.	Sample Wt	% Collected <sup>c</sup>	Tocopherol <sup>d</sup> Concentration
1	0.54 g	1.41	2,420
2	0.89 g	3.73	2,420
3	1.49 g	7.64	975
4	1.05 g	10.38	530
5	2.86 g	17.86	510

Extraction conditions: Sample weight = 38.23 g

Fractions 1-4: 3,500 psi, 80°C

Fraction 5: 12,000 psi, 80°C

<sup>c</sup>Based on weight of the original sample

<sup>d</sup>In µg/g

Similarly, one can enrich a component in an extracted matrix by varying either the extraction pressure or time. The data for tocopherol enrichment in a soybean oil extract in Table IV clearly shows that enrichment of this minor, but important, component in the soybean oil matrix is favored by conducting the extraction at lower pressures. In this case, total separation of the oil and tocopherol was not necessary, since the end-use application of this extract required that it be blended into a lipid-based product matrix.

### Tailoring Extracts for Cosmetic Applications

The properties of an extract derived from a natural product can be controlled by employing SF processing. Such properties as melting point, color and odor of the extract can all be modified by adjusting the SFE process. An excellent example of this concept is shown in Table V. Here, SC-CO<sub>2</sub> has been used to fractionate wool grease into several constituent fractions, all having different melting points.

The fractions in this case were each collected at intervals consisting of the passage of 6 lbs. of CO<sub>2</sub> held at 8000 psi and 80°C. Hence, this fractionation is based on differences in processing time, rather than pressure or temperature. Besides having different melting points, these extract fractions differ in their cholesterol content and odoriferous properties.

Control of product color through SF processing is also possible. As noted previously, SF-processed oils tend to be lighter in color than the starting substrate. Variation is quite high.

Our experience at NCAUR has been predominately with food-related products. However, the extraction principles involved are equally applicable to processing cosmetic raw materials. Both SF-derived oils or treated substrates, such as meals, germs, or starches, have improved or marginally better flavor scores from organoleptic taste panels.<sup>16</sup> The extraction pressure and temperature, coupled with the moisture content of the substrate, are critical extraction parameters for obtaining a good flavor score.

SFE is an excellent technique for concentrating aroma components in a lipophilic base material. Extractions performed on the recycle system described in Figure 1 have permitted the concentration of food aromas in a coextracted oil. The aroma constituents are extracted from the substrate placed in vessel A-C and collected and concentrated continuously in the receiver vessel as the CO<sub>2</sub> is recycled in the extraction system.

Experiments using peanut oil have shown that the SF-derived aroma concentrate has many components not present in the pressed product. Major flavor notes are enhanced many-fold in the oil base. The concentrating effect which takes place in the receiver vessel could be viewed as the SF form of "enfleurage."<sup>17</sup>

On the other end of the extraction scale, recent work in extract color is not only a function of extraction pressure and temperature, but also processing time. Recent experiments at NCAUR for the SF-refining of solvent-extracted seed oils, using countercurrent contact of the extraction gas with the seed oil in a packed-bed extractor, have shown that a lighter-colored oil is achieved during the earlier portion of the extraction.

**Table V. Melting points of extracted wool grease fractions<sup>a</sup>**

Fraction	Melting Point (°C)
Wool grease	44.5
Fraction 1	26.1
Fraction 2	35.3
Fraction 3	34.5
Fraction 4	34.3
Unextracted Residue	47.5

<sup>a</sup>Data courtesy of M. Cygnarowicz-Provost, ERRC-USDA

Both pressure/temperature and extraction time have been used by Favati et al.<sup>13</sup> to produce colored extracts, in a vegetable oil base, from alfalfa leaf protein concentrate. Variation of the three parameters changes the ratio of carotenoids to xanthophylls in the extract, thereby producing natural colorant mixtures of different hues.

A more dramatic effect can be seen in the extraction of avocado oil with SC-CO<sub>2</sub>. Using the conditions cited in Table VI, a high yield of green oil may be obtained from freeze-dried avocado pulp. However, conducting the extraction at a pressure lower than 10,000 psi produces a yellow oil that is similar in color to a refined avocado oil.<sup>14</sup>

Similarly, one can modify the odor/flavor characteristics of cosmetic raw materials by treatment with a SF. Examples of fragrance isolations that have been reported in the literature<sup>15</sup> have utilized relatively low extraction pressures, since the volatility of the odoriferous compounds in our laboratory has shown that micro-scale SFE coupled with such separation techniques as gas and SF chromatography are powerful diagnostic tools for locating the source of odoriferous volatiles in plant matter. Coupled SFE/chromatography on the calyces, resin sacs, and leaves of *Dalea spinosa* (the smoke tree), a desert botanical, has permitted the characterization of the SF-derived extractives from these plant parts.<sup>18</sup> Such information can be valuable for the scaled-up SFE of this botanical specie, which emits a distinct musk-like odor of value to perfumers.

## Summary

This brief review describes the potential of SFE not only for isolation of raw materials of value to the cosmetic industry, but for tailoring the physical and chemical properties of extracted products. Not only can processing with supercritical fluids change the melting point, color, and odor of the end extract, but it can accomplish such a task without introducing solvent residuals into the cosmetic ingredient. This, coupled with the ecological compatibility of the process, suggests a number of uses in the cosmetic formulating industry. The ever-increasing number of plant facilities devoted to SFE confirms its viability as a materials-processing option.

## References

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**Table VI. Supercritical CO<sub>2</sub> extraction of avocado oil**

Extraction conditions:	
Pressure	11,000 psi
Temperature	70°C
Time	24 hr
Moisture content, %	3.4
Residual oil, %	5.3
Oil recovered, g/100g of oil bearing material	58.2
Description	green <sup>f</sup> oil

<sup>f</sup>A green oil was also produced at 10,000 psi and 80°C. Below 10,000 psi and 70°C, a yellow oil was obtained.

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